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Remarks:

A request for correction of an expression in the description, the claims and the abstract has been filed pursuant to Rule 88 EPC. A decision on the request will be taken during the proceedings before the Examining Division (Guidelines for Examination in the EPO, A-V, 3.).

**(54) Photocatalytic bleaching agent for teeth and method**

(57) A method for bleaching teeth comprises steps of applying a solution containing nitrogen-doped titanium oxide powder on a surface of teeth, and irradiating the applied part with light to bleach the teeth based on a photocatalytic action thus produced, and a bleaching agent for teeth suitable for carrying out the method comprises a solution containing nitrogen-doped titanium oxide powder, in which the nitrogen-doped titanium oxide is preferably a photocatalytic substance having a Ti-O-N structure having a titanium oxide crystalline lattice containing nitrogen and exhibiting a photocatalytic action in

a visible light region, the bleaching agent contains preferably 0.01 to 5% by weight of the nitrogen-doped titanium oxide powder, the nitrogen-doped titanium oxide powder has a specific surface area of from 10 to 500 m<sup>2</sup>/g, the solution contains water and/or an alcohol as a solvent, and the bleaching agent further contains preferably 0.5 to 20% by weight of a thickener, 1 to 20% by weight of hydrogen peroxide, and 2 to 45% by weight of urea peroxide.

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## Description

[0001] The present invention relates to a method for bleaching teeth for removing pigments deposited on teeth (coloration and discoloration of teeth) by an action of a photocatalyst, and a bleaching agent for teeth suitable for carrying out the method for bleaching teeth. More specifically, it relates to a method for bleaching teeth by applying a bleaching agent for teeth having a photocatalytic activity on a surface of teeth, and irradiating the applied part with light to bleach the teeth based on a photocatalytic action thus produced, and a bleaching agent for teeth useful for carrying out the method for bleaching teeth comprising a solution containing nitrogen-doped titanium oxide powder that produces a photocatalytic action upon irradiation with light.

[0002] It is generally considered that whiteness of teeth is an important factor of beautification, and there are strong demands for whitening teeth centrally in young women to produce increasing cases of desiring bleach of teeth. As a method for bleaching teeth, a method using a hydrogen peroxide aqueous ( $H_2O_2$ ) solution has been generally practiced.

[0003] The conventional bleaching method has been generally practiced as a method for bleaching teeth in that light and heat are applied to a hydrogen peroxide aqueous solution (concentration: about 30% by weight), in which gauze impregnated with the hydrogen peroxide aqueous solution is placed on a labial surface of teeth and irradiated with light by lamp for about 30 minutes. In this method, the lamps are made close to the teeth as much as possible and the hydrogen peroxide aqueous solution is supplied by about 5 minutes to prevent the gauze from drying.

[0004] There are also a method of repeating such an operation six to eight times instead of the irradiation with light that a high frequency electric current is applied for 1 second with a spoon-shaped chip equipped on a high frequency electric cautery knife and then the operation is suspended for 8 seconds, and a method of directly applying a solution (paste) formed by mixing a thickener with a hydrogen peroxide aqueous solution to teeth instead of impregnation into gauze. However, a hydrogen peroxide aqueous solution having a concentration exceeding 25% by weight is necessarily handled carefully due to the strong corrosion nature thereof.

[0005] Many other bleaching agents and bleaching methods using a hydrogen peroxide aqueous solution having a concentration of 20 to 35% combined with other equipments and other agents have been proposed, such as a bleaching method of using a mixed solution of hydrochloric acid, a hydrogen peroxide aqueous solution and diethyl ether as an agent (modified McInnes bleaching method), a method of using a paste formed by kneading powder of sodium perborate and a 30% by weight hydrogen peroxide aqueous solution as an agent (working bleach method), a bleaching agent for teeth formed by mixing a hydrogen peroxide aqueous solution and orthophosphoric acid and a bleaching method using the same (JP-A-8-143436), a bleaching agent formed by mixing a hydrogen peroxide aqueous solution and silicic anhydride and a method for bleaching vital teeth of coating the bleaching agent (JP-A-5-320033), and a dental bleaching composition containing a dental bleaching agent (such as urea hydrogen peroxide, hydrogen carbamide peroxide and carbamide peroxide) and a matrix material (such as carboxymethylene) and a method for bleaching teeth using the same (JP-A-8-113520). However, these methods involve the same problems as in the foregoing methods from the standpoint of the use of hydrogen peroxide in a high concentration. There is also a bleaching method using urea peroxide in a concentration of about 10% by weight, instead of a hydrogen peroxide aqueous solution, as an example of bleaching methods that have been practiced in the United States, but no sufficient results have been obtained.

[0006] As a bleaching agent and a bleaching method for teeth using no hydrogen peroxide aqueous solution in a high concentration as described in the foregoing, such a method for bleaching teeth is also proposed that uses titanium dioxide having a photocatalytic action and, depending on necessity, a hydrogen peroxide aqueous solution. However, the conventional bleaching method and bleaching agent using titanium dioxide has such a defect that they exhibit substantially no catalytic action with respect to visible light while they exhibit catalytic action with respect to ultraviolet light (generally having a wavelength of less than 380 nm) owing to the band gap of the titanium dioxide used (Eg for the anatase type titanium dioxide is 3.2 eV). Ultraviolet light is malefic to a human body and thus is not suitable for long-term irradiation in an oral cavity, and therefore, it has been demanded to develop a novel method for bleaching teeth and a novel bleaching agent for teeth using a substance that effectively exhibits a photocatalytic action by using a light source containing substantially no ultraviolet light, such as a dental light source.

[0007] An object of the present invention is to provide a method for bleaching teeth and a bleaching agent for teeth that exhibit high bleaching effect with visible light.

[0008] As a result of earnest investigations made by the inventors for solving the problems associated with the conventional techniques, it has been found that in the case where nitrogen-doped (doped) titanium oxide as mentioned below is used, the absorption edge of the light absorption spectrum can be shifted to a long wavelength side in comparison to the conventional case using titanium dioxide, so as to exhibit a photocatalytic activity with light having a longer wavelength, whereby a method for bleaching teeth and a bleaching agent for teeth exhibiting a high catalytic activity with visible light can be obtained, and thus the invention has been completed. Examples of the nitrogen-doped titanium oxide include those obtained in such a manner that titanium dioxide excellent in stability to water and acids is basically used as a photocatalytic substance, and it is subjected to one or more of these operations, i.e., a part of the

oxygen site of titanium dioxide is substituted with a nitrogen atom as proposed in WO01/10552 by the inventors, a nitrogen atom is doped among the lattice of titanium dioxide crystals, and a nitrogen atom is doped on the crystalline boundaries of titanium dioxide.

[0009] That is, the present invention relates to a method for bleaching teeth comprising steps of applying a solution containing nitrogen-deeped titanium oxide powder on a surface of teeth, and irradiating the applied part with light to bleach the teeth based on a photocatalytic action thus produced, and it also relates to a bleaching agent for teeth comprising a solution containing nitrogen-deeped titanium oxide powder that is suitable for carrying out the method for bleaching teeth. It is preferred in the method for bleaching teeth that light thus irradiated is visible light. It is preferred in the bleaching agent for teeth that the nitrogen-deeped titanium oxide is a photocatalytic substance having a Ti-O-N structure having a titanium oxide crystalline lattice containing nitrogen and exhibiting a photocatalytic action in a visible light region, and in this case, it is further preferred that the nitrogen-deeped titanium oxide contains titanium oxide containing no nitrogen on the outer surface thereof, a surface of the nitrogen-deeped titanium oxide comprises a ceramic carried in an island form, needle form or a mesh form, and the surface of the nitrogen-deeped titanium oxide carries a charge separation substance. It is also preferred in the bleaching agent for teeth that the bleaching agent contains from 0.01 to 5% by weight of the nitrogen-deeped titanium oxide powder, the nitrogen-deeped titanium oxide powder has a specific surface area of 10 to 500 m<sup>2</sup>/g, the solution contains water and/or an alcohol or a polyhydric alcohol as a solvent, the bleaching agent further contains 0.5 to 20% by weight of a thickener, the bleaching agent further contains 1 to 20% by weight of hydrogen peroxide, and the bleaching agent further contains 2 to 45% by weight of urea peroxide.

[0010] The bleaching agent for teeth according to the present invention has a solution containing nitrogen-deeped titanium oxide powder, and preferably a solution containing nitrogen-deeped titanium oxide in an amount of 0.01 to 5% by weight based on the total amount of the bleaching agent for teeth. The nitrogen-deeped titanium oxide powder is preferably a photocatalytic substance having a Ti-O-N structure having a titanium oxide crystalline lattice containing nitrogen and exhibiting a photocatalytic action in a visible light region as proposed in WO01/10552.

[0011] The nitrogen-deeped titanium oxide may be nitrogen-deeped titanium oxide shown in WO01/10552 and can be produced by heat treating titanium oxide or hydrated titanium oxide in an atmosphere containing ammonia gas, an atmosphere containing a nitrogen gas, or a mixed atmosphere of a nitrogen gas and a hydrogen gas. The nitrogen-deeped titanium oxide can also be produced by mixing and agitating powder of titanium oxide and urea and then heating the mixture as shown in JP-A-2002-154823.

[0012] The nitrogen-deeped titanium oxide used in the present invention may contain titanium oxide containing no nitrogen on the outer surface thereof as shown in WO01/10552. According to the configuration, the hydrophilicity of the powder surface is improved, and the bleaching capability in wet conditions can be improved.

[0013] The nitrogen-deeped titanium oxide used in the present invention may comprise ceramics carried in an island form, needle form or a mesh form on the surface thereof, as shown in WO01/10552. Examples of the ceramics include at least one selected from alumina, silica, zirconia, magnesia, calcia, calciumphosphate, apatite, amorphous titanium oxide and a fluorine resin. The ceramics are liable to absorb stains deposited on teeth and can improve the bleaching capability.

[0014] As the nitrogen-deeped titanium oxide used in the present invention, such kinds of titanium dioxide may be used that are formed in such a manner that titanium of the nitrogen-deeped titanium oxide is substituted with at least one kind selected from vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, ruthenium, rhodium, rhenium, osmium, palladium, platinum, iridium, niobium and molybdenum, or at least one of these elements is doped among the lattice of titanium dioxide crystals or on the crystalline boundaries of polycrystalline aggregates of titanium dioxide, as shown in JP-A-2001-205104. The absorption edge of the light absorption spectrum of these kinds of nitrogen-deeped titanium oxide can be shifted to a long wavelength side in comparison to the conventional case using titanium dioxide, so as to exhibit a photocatalytic activity with light having a longer wavelength.

[0015] The nitrogen-deeped titanium oxide used in the present invention may carry a charge separation substance on the surface thereof as shown in JP-A-2001-205103. Examples of the charge separation substance include at least one selected from Pt, Pd, Ni, RuO<sub>x</sub>, NiO<sub>x</sub>, SnO<sub>x</sub>, Al<sub>x</sub>O<sub>y</sub> and ZnO<sub>x</sub>. The charge separation substance scavenges electrons or positive holes, and thus recombination of electrons and positive holes is effectively prevented. Therefore, the photocatalytic reaction can be carried out in a more effective manner to improve the bleaching capability.

[0016] In the case where the mixing amount of the nitrogen-deeped titanium oxide is less than 0.01% by weight, there is such a tendency that the effect as a photocatalyst is difficult to be obtained, and in the case where it is mixed in an amount exceeding 5% by weight, there is such a possibility that the bleaching agent for teeth is deteriorated in transparency, and thus the bleaching capability is reduced due to reduction in light transmittance. The mixing amount of the nitrogen-deeped titanium oxide is more preferably 0.01 to 2% by weight. The specific surface area of the nitrogen-deeped titanium oxide powder is preferably 10 to 500 m<sup>2</sup>/g, and nitrogen-deeped titanium oxide powder having a specific surface area less than 10 m<sup>2</sup>/g has such a possibility of decreasing the catalytic activity, whereas there is a strong tendency that production, procurement and use of nitrogen-deeped titanium oxide powder having a specific

surface area exceeding 500 m<sup>2</sup>/g are difficult.

[0017] In the bleaching agent for teeth of the present invention, in order that the nitrogen-deeped titanium oxide powder is effectively made in contact with teeth, it is necessary that the bleaching agent for teeth is formed into a solution (including a paste) by using a solvent. The solvent for the solution is preferably water and/or an alcohol. Among these, water is the most preferred from the standpoint of reactivity of the nitrogen-deeped titanium oxide, and ethanol and a polyhydric alcohol are the most preferred from the standpoint of the application operation of the bleaching agent for teeth to teeth. In the polyhydric alcohol, glycerin, ethylene glycol, diethylene glycol, polyethylene glycol, propylene glycol, polypropylene glycol, sorbitol, mannitol and mixtures thereof are preferred since they are excellent in safety and good in affinity to teeth.

[0018] It is preferred that the bleaching agent of the present invention further contains a thickener in an amount of 0.5 to 20% by weight based on the total amount of the bleaching agent for teeth in order that the nitrogen-deeped titanium oxide is easily coated on teeth and is effectively stayed on the tooth surface. The mixing amount of the thickener of less than 0.5% by weight is difficult to obtain effect of mixing it, and mixing in an amount exceeding 20% by weight causes a possibility of deterioration in operability on application to teeth due to a too high viscosity of the solution. The thickener used in the present invention may be those thickeners that have been used in the field of dentistry without particular limitation, and examples thereof include a synthetic additive, such as cellulose sodium glycolate, sodium alginate, alginic acid propylene glycol ester, sodium carboxymethyl cellulose, calcium carboxymethyl cellulose, starch sodium glycolate, starch sodium phosphate ester, sodium polyacrylate, methyl cellulose, hydroxypropyl cellulose and polyvinyl pyrrolidone, a natural thickener, such as guar gum, tara gum, tamarind seed gum, gum arabic, tragant gum, karaya gum, alginic acid, carrageenan, xanthan gum, gellan gum, curdlan, chitin, chitosan, and chitosamine, and an inorganic thickener, such as calcium carbonate, calcium silicate, magnesium silicate, magnesium sodium silicate, silica powder, amorphous hydrous silicic acid and fumed silica. It has been confirmed by experimentation that the suitable viscosity obtained with the thickener is preferably in a range from 0.3 to 10 Pa.s (at 25°C). The mixing amount of the thickener for obtaining the viscosity in that range varies within the foregoing range depending on the species of the thickener. The mixing amount may be only about 0.5 to 8% for cellulose sodium glycolate or the like having a large thickening effect, whereas it is necessarily 15% or more for methyl cellulose or the like, and the suitable mixing amount is determined individually for the respective thickeners.

[0019] The bleaching agent for teeth according to the present invention may further contain hydrogen peroxide in an amount of 1 to 20% by weight based on the total amount of the bleaching agent for teeth in order to obtain bleaching effect by synergistic effect of the nitrogen-deeped titanium oxide and hydrogen peroxide in a low concentration. In the case where the mixing amount of hydrogen peroxide is less than 1% by weight, the effect of hydrogen peroxide is difficult to be obtained, and in the case where it is added in an amount exceeding 20% by weight, there is possible adverse affect to a living body due to corrosive nature of hydrogen peroxide. Upon irradiating the nitrogen-deeped titanium oxide powder with light, electrons and positive holes are generated, and they are reacted with hydrogen peroxide to form active oxygen. Active oxygen has larger oxidation power than ozone and can oxidatively decompose almost all organic substances to carbon dioxide gas. Even in the case of n-type semiconductor titanium oxide powder having a relatively large band gap, active oxygen having strong oxidation power is easily produced by irradiation with light upon using, for example, as a solution with a 3% hydrogen peroxide aqueous solution, and thus such factors as charge separation, mobility of electrons and positive holes, and reactivity with protons and hydroxyl groups, are increased in comparison to the sole use thereof, whereby the synergistic effect can be exerted correlatively with the oxidation action of the hydrogen peroxide aqueous solution itself.

[0020] The bleaching agent for teeth according to the present invention may further contain urea peroxide in an amount of 2 to 45% by weight based on the total amount of the bleaching agent for teeth in order to obtain stronger bleaching effect. In the case where the mixing amount of urea peroxide is less than 2% by weight, the effect of addition of urea peroxide is difficult to be obtained, and in the case where it is added in an amount exceeding 45% by weight, there is such a possibility that safety is lowered due to the urea peroxide.

[0021] The bleaching agent for teeth according to the present invention is a solution containing nitrogen-deeped titanium oxide, and for example, can be used in the form of solution as it is. In the case where hydrogen peroxide and/or urea peroxide is mixed, the mode of provision of them is not particularly limited, and for example, it is possible that the additional components are separately prepared and accompanied to the solution, and they are then mixed at a time of use. In addition, the bleaching agent for teeth according to the present invention may contain ordinary additives, such as a sweetener, a perfume and an antiseptic.

[0022] In the method for bleaching teeth according to the present invention, the solution containing nitrogen-deeped titanium oxide powder is applied to the surface of teeth. As one of the simplest methods for applying the solution on the surface of teeth, the solution containing nitrogen-deeped titanium oxide powder having a photocatalytic action as the bleaching agent for teeth is directly coated on teeth by using a brush or the like. Other examples thereof include such a method that cloth, paper, glass cloth, ceramic paper, organic gel or inorganic gel is impregnated with the bleaching agent for teeth and attached to the surface of teeth, followed by irradiating with light. Moreover, any appropriate

methods can also be employed, such as a method, in which the bleaching agent for teeth is retained by a suitable carrier, such as a carrier in the form of a mouse guard, and it is outfit on teeth or a tooth raw to attach the solution to teeth.

[0023] Examples of a light source (lighting equipment) of light used in the present invention include an incandescent lamp, a fluorescent lamp, a halogen lamp, a xenon lamp, a mercury lamp and an UV lamp, and in particular, an LED (light emitting diode) and a semiconductor laser lamp (pen light) are preferred from the standpoint of safety, handiness and bleaching effect. The light to be irradiated is preferably that containing a large amount of light having a short wavelength, such as an ultraviolet ray, from the standpoint of generation of active oxygen by the photocatalytic action and the oxidation action thereof, but because an ultraviolet ray is harmful for a human body as causing inflammation and cancer, the use of visible light is preferred from the standpoint of safety with the use of violet and/or blue light having larger energy being most preferred.

[0024] The method for bleaching teeth according to the present invention can be carried out by repeating several times such an operation that the bleaching agent for teeth, which is the solution containing nitrogen-deeped titanium oxide having photocatalytic action, is applied to the surface of teeth, which is then irradiated with light. The number of repetitions of the application and irradiation operations may be appropriately adjusted depending on the extent of discoloration of the teeth. The application and light irradiation operations may be generally carried out by applying a fresh solution on the teeth with an interval of about 15 to 20 minutes, and the interval and the frequency thereof may be appropriately determined depending on the conditions of the teeth and the formulation of the bleaching agent for teeth. The method for bleaching teeth according to the present invention is effective for bleaching both demyelinated teeth and myelinated teeth and exerts remarkable effect on bleaching the teeth in a simple and safe manner.

[0025] The invention will be specifically described with reference to the following examples, but the present invention is not construed as being limited thereto.

#### **Production of Bleaching Agent for Teeth**

[0026] As shown in Tables 1 to 13, nitrogen-deeped titanium oxide powder was mixed and dispersed in one or a plurality of water, ethanol, glycerin, polyethylene glycol (weight average molecular weight: 200) and sorbitol as a solvent, and then a small amount of a thickener (magnesium sodium silicate and silica fine powder (Aerosil R972, a trade name, produced by Nippon Aerosil Co., Ltd.)) was added thereto depending on necessity, so as to produce bleaching agents for teeth, which were then sealed in light shielding containers.

[0027] The following kinds of nitrogen-deeped titanium oxide powder were used.

(Powder A)

[0028] As shown in JP-A-2002-154823, commercially available titanium dioxide powder (ST-01, a trade name, produced by Ishihara Sangyo Kaisha, Ltd.) and urea were mixed and agitated, and then subjected to a heat treatment at 450°C for 30 minutes to produce powder A having a specific surface area of 280 m<sup>2</sup>/g.

(Powder B)

[0029] As shown in WO01/10552, commercially available titanium dioxide powder (ST-01, a trade name, produced by Ishihara Sangyo Kaisha, Ltd.) was subjected to a heat treatment in a mixed gas atmosphere of argon gas and ammonia gas at 600°C for 3 hours to produce powder B having a specific surface area of 67 m<sup>2</sup>/g.

(Powder A-Ap)

[0030] Apatite was carried on the surface of the powder A by the method shown in WO01/10552 to produce powder A-Ap.

(Powder B-Ap)

[0031] Apatite was carried on the surface of the powder B by the method shown in WO01/10552 to produce powder B-Ap.

(Powder A-Pt)

[0032] Platinum was carried on the surface of the powder A by the method shown in JP-A-2001-205103 to produce powder A-Pt.

(Powder B-Pt)

[0033] Platinum was carried on the surface of the powder B by the method shown in JP-A-2001-205103 to produce powder B-Pt.

5 [0034] In the case of a combination of such components that a metallic component (platinum in the examples) in the nitrogen-deeped titanium oxide and hydrogen peroxide were to start to react with each other immediately after mixing, the components were produced as separated to two or more portions, and the two or more portions of the bleaching agent for teeth were mixed immediately before application to teeth (Examples 19, 25, 26, 45, 51 and 52). In the case where the components were a combination of urea peroxide and water to be mixed, they were produced as separated  
10 to two or more portions since urea peroxide were to start to decompose by water immediately after mixing urea peroxide with water, and the two or more portions of the bleaching agent for teeth were mixed immediately before application to teeth (Examples 26 and 52). In the bleaching agent for teeth constituted of two or more portions in the examples, the same amounts (by weight) of the portions were mixed. The case using titanium dioxide powder (ST-01, a trade name, produced by Ishihara Sangyo Kaisha, Ltd.) as conventional titanium dioxide powder was designated as Comparative Example 1.  
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TABLE 1 (% by weight)

	Example 1	Example 2	Example 3	Example 4	Example 5
Powder A	0.05	0.05	0.05	0.10	0.8
Water	balance	balance		balance	balance
Ethanol		40			
Glycerin			balance	40	
Polyethylene glycol					40
Sodium magnesium silicate	3	3			
Silica fine powder			5	5	5
Total	100	100	100	100	100

TABLE 2 (% by weight)

	Example 6	Example 7	Example 8	Example 9	Example 10
Powder A-Pt	0.05	0.05	0.05	0.10	0.8
Water	balance	balance		balance	balance
Ethanol	10	40			10
Glycerin			balance	40	
Polyethylene glycol			20		40
Sodium magnesium silicate	3	3			
Silica fine powder				5	10
Total	100	100	100	100	100

TABLE 3 (% by weight)

	Example 11	Example 12	Example 13	Example 14	Example 15
Powder A-AP	0.05	0.05	0.05	0.10	0.5
Water	balance	balance		balance	balance
Ethanol		40		10	
Glycerin			balance	35	
Polyethylene glycol					35
Sodium magnesium silicate	10	5			
Silica fine powder			1	3	5
Total	100	100	100	100	100

TABLE 4 (% by weight)

	Example 16	Example 17	Example 18	Example 19	
Powder A	0.05	0.05			0.05
Powder A-PT				0.05	
Powder A-AP			0.05		
Water	balance	balance	balance	balance	balance
Hydrogen peroxide	2.91	4.85	2.91		2.91
Sodium magnesium silicate	3		5	3	3
Total	100	100	100	100	100



TABLE 5 (% by weight)

	Example 20	Example 21	Example 22	Example 23	Example 24
Powder A	0.05	0.10			
Powder A-Pt			0.05	0.10	0.8
Urea peroxide	10	15	5	20	15
Ethanol			balance		5
Glycerin		balance		35	balance
Diethylene glycol			10	balance	
Sorbitol	balance				
Silica fine powder	7		10	5	12
Total	100	100	100	100	100

TABLE 6 (% by weight)

	Example 25		Example 26	
Powder A-Pt	0.05		1	
Hydrogen peroxide		2.91		10
Urea peroxide	20		30	
Water		balance		balance
Ethanol		10	40	15
Glycerin	balance			balance
Diethylene glycol			balance	
Magnesium sodium silicate		3		3
Silica fine powder	5		7	3
Total	100	100	100	100

TABLE 7 (% by weight)

	Example 27	Example 28	Example 29	Example 30	Example 31
Powder B	0.2	0.2	0.2	0.5	1.0
Water	balance	balance		balance	balance
Ethanol		40			
Glycerin			balance	40	
Polyethylene glycol					40
Magnesium sodium silicate	3	3			
Silica fine powder			5	5	5
Total	100	100	100	100	100

TABLE 8 (% by weight)

	Example 32	Example 33	Example 34	Example 35	Example 36
Powder B-Pt	0.2	0.2	0.2	0.2	1.0
Water	balance	balance	balance	balance	balance
Ethanol	10	40	balance	40	10
Glycerin			20		40
Polyethylene glycol					
Magnesium sodium silicate	3	3			
Silica fine powder				5	10
Total	100	100	100	100	100

TABLE 9 (% by weight)

	Example 37	Example 38	Example 39	Example 40	Example 41
Powder B-AP	0.05	0.05	0.05	0.10	0.5
Water	balance	balance	balance	balance	balance
Ethanol		40		10	
Glycerin			balance	35	
Polyethylene glycol					35
Magnesium sodium silicate	10	5			
Silica fine powder			1	3	5
Total	100	100	100	100	100

TABLE 10 (% by weight)

	Example 42	Example 43	Example 44	Example 45
Powder B	0.2	0.2		0.2
Powder B-Pt				0.2
Powder B-AP			0.2	
Water	balance	balance	balance	balance
Hydrogen peroxide	2.91	4.85	2.91	2.91
Sodium magnesium silicate	3		5	3
Total	100	100	100	100

TABLE 11 (% by weight)

	Example 46	Example 47	Example 48	Example 49	Example 50
Powder B	0.2	0.5			
Powder B-Pt			0.2	0.5	1.0
Urea peroxide	10	15	5	20	15
Ethanol			balance		5
Glycerin		balance		35	balance
Diethylene glycol			10	balance	
Sorbitol	balance				
Silica fine powder	7		10	5	12
Total	100	100	100	100	100

TABLE 12 (% by weight)

	Example 51		Example 52	
	0.2	2.91	2.0	
Powder B-Pt				
Hydrogen peroxide				10
Urea peroxide	20		30	
Water		balance		balance
Ethanol		10	40	35
Glycerin	balance			balance
Diethylene glycol			balance	
Magnesium sodium silicate		3		3
Silica fine powder	5		7	3
Total	100	100	100	100

TABLE 13 (% by weight)

	Comparative Example 1		Comparative Example 2	
	0.05			
Conventional titanium dioxide powder				
Hydrogen peroxide			35	
Water		balance	balance	
Ethanol			10	
Magnesium sodium silicate	5		2	
Silica fine powder			5	
Total	100	100	100	

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(Method of Using)

[0035]

(1) As pretreatment, dental plaque, dental scale, tar and the like on the surface of the objective tooth were removed with an ultrasonic scaler.

(2) The surface of the tooth was cleaned with a rubber cup or the like in an ordinary method and then dried.

(3) A simple moisture prevention treatment was carried out.

(4) The bleaching agents for teeth of the examples and the comparative examples were coated on the surface of the tooth and light irradiation was carried out by using a dental visible light irradiator (Labolight LVII, a trade name, produced by GC Corporation). The irradiation period was 5 minutes per once, and the distance from the surface of the tooth to the irradiator was about 1 cm.

(5) Application of a fresh bleaching agent for teeth and irradiation with light were repeated with an interval of 15 to 20 minutes.

(6) The effect of bleaching was evaluated in such a manner that colors of the tooth before and after bleaching were pictured with a video camera. The pictures thus obtained were presented to the patients, and evaluation was made in the following three grades.

+++ The patient was especially satisfied.

++ Bleaching effect somewhat satisfying the patient was obtained.

+ Bleaching effect was found, but discoloration somewhat remained, and the patient was not satisfied.

[0036] The results of the evaluation are shown in Table 14 below.

(Method of Using 2)

[0037] The surface of the tooth was cleaned in the foregoing manner. Paper ceramics (produced by Noritake Co., Ltd.) was impregnated with the bleaching agents for teeth in Examples 8, 17, 21, 34, 43 and 47, and attached to the surface of the tooth followed by irradiating with visible light.

TABLE 14

	Site	Accumulated irradiation time (minute)	Effect
Example 1	maxilla left 1	90	+++
Example 2	maxilla left 2	100	+++
Example 3	maxilla right 1	80	+++
Example 4	maxilla left 3	90	+++
Example 5	maxilla right 2	100	++
Example 6	mandible left 1	70	+++
Example 7	mandible left 2	65	+++
Example 8	maxilla right 3	80	+++
Example 9	maxilla right 3	90	+++
Example 10	maxilla left 2	80	+++
Example 11	maxilla right 2	120	+++
Example 12	mandible left 3	100	+++
Example 13	mandible left 2	90	++
Example 14	mandible right 1	90	+++
Example 15	mandible right 2	80	+++
Example 16	mandible left 2	100	++
Example 17	mandible left 1	90	++

TABLE 14 (continued)

	Site	Accumulated irradiation time (minute)	Effect
Example 18	maxilla left 1	120	++
Example 19	maxilla right 2	100	++
Example 20	mandible left 1	90	++
Example 21	mandible left 2	60	+++
Example 22	maxilla right 3	50	+++
Example 23	maxilla right 3	30	+++
Example 24	maxilla left 2	55	+++
Example 25	maxilla left 2	65	+++
Example 26	maxilla right 1	70	+++
Example 27	mandible left 2	100	+++
Example 28	maxilla left 1	85	+++
Example 29	mandible right 2	80	+++
Example 30	mandible left 3	95	+++
Example 31	maxilla right 2	90	++
Example 32	maxilla left 1	80	++
Example 33	maxilla left 1	70	+++
Example 34	maxilla right 2	90	+++
Example 35	maxilla right 3	75	+++
Example 36	maxilla left 1	75	++
Example 37	maxilla right 2	115	+++
Example 38	mandible left 3	110	+++
Example 39	maxilla left 1	70	+++
Example 40	maxilla right 2	75	+++
Example 41	mandible right 1	85	+++
Example 42	mandible left 2	105	++
Example 43	maxilla left 1	95	++
Example 44	mandible left 3	110	++
Example 45	maxilla right 2	90	++
Example 46	mandible left 2	95	++
Example 47	mandible left 2	55	+++
Example 48	maxilla right 2	45	+++
Example 49	maxilla right 3	40	+++
Example 50	mandible left 1	45	+++
Example 51	maxilla left 2	50	+++
Example 52	maxilla right 1	65	+++
Comparative Example 1	maxilla right 3	120	+
Comparative Example 2	maxilla left 2	100	++

[0038] It was confirmed as apparent from the foregoing results that the method for bleaching teeth and the bleaching agent for teeth according to the present invention exerted high bleaching effect even with irradiation of visible light, and thus bleach of teeth could be carried out by using no hydrogen peroxide in a high concentration exceeding 30% by weight as in Comparative Example 2.

[0039] As described in the foregoing in detail, the method for bleaching teeth and the bleaching agent for teeth according to the present invention uses nitrogen-deeped titanium oxide, whereby the absorption edge of the light absorption spectrum can be shifted to a long wavelength side in comparison to the conventional case using titanium dioxide, so as to exhibit a photocatalytic activity with light having a longer wavelength. As a result, such a bleaching agent for teeth excellent in performance is provided that exhibits high bleaching effect even by using a dental visible light irradiator, which is generally used in dentistry, and such a method for bleaching teeth using the bleaching agent for teeth is also provided that can effectively bleach teeth with enjoying the effects of the bleaching agent. The nitrogen-deeped titanium oxide can be obtained in such a manner that titanium dioxide excellent in stability to water and acids is basically used as a photocatalytic substance, and it is subjected to one or more of these operations, i.e., a part of the oxygen site of titanium dioxide is substituted with a nitrogen atom, a nitrogen atom is doped among the lattice of titanium dioxide crystals, and a nitrogen atom is doped on the crystalline boundaries of titanium dioxide. Accordingly, the present invention greatly contributes to the field of bleach of teeth.

### Claims

1. A method for bleaching teeth comprising steps of applying a solution containing nitrogen-deeped titanium oxide powder on a surface of teeth, and irradiating the applied part with light to bleach the teeth based on a photocatalytic action thus produced.
2. A method for bleaching teeth as claimed in claim 1, wherein visible light is irradiated as the light.
3. A bleaching agent for teeth comprising a solution containing nitrogen-deeped titanium oxide powder, which is attached to a surface of teeth and irradiated with light to bleach the teeth based on a photocatalytic action thus produced.
4. A bleaching agent for teeth as claimed in claim 3, wherein the nitrogen-deeped titanium oxide is a photocatalytic substance having a Ti-O-N structure having a titanium oxide crystalline lattice containing nitrogen and exhibiting a photocatalytic action in a visible light region.
5. A bleaching agent for teeth as claimed in claim 4, wherein the nitrogen-deeped titanium oxide contains titanium oxide containing no nitrogen on the outer surface thereof.
6. A bleaching agent for teeth as claimed in claim 4, wherein a surface of the nitrogen-deeped titanium oxide comprises a ceramic carried in an island form, needle form or a mesh form.
7. A bleaching agent for teeth as claimed in claim 4, wherein a surface of the nitrogen-deeped titanium oxide carries a charge separation substance.
8. A bleaching agent for teeth as claimed in any one of claims 3 to 7, wherein the bleaching agent for teeth contains 0.01 to 5% by weight of the nitrogen-deeped titanium oxide powder.
9. A bleaching agent for teeth as claimed in any one of claims 3 to 8, wherein the nitrogen-deeped titanium oxide powder has a specific surface area of 10 to 500 m<sup>2</sup>/g.
10. A bleaching agent for teeth as claimed in any one of claims 3 to 9, wherein the solution contains water and/or an alcohol as a solvent.
11. A bleaching agent for teeth as claimed in claim 10, wherein the alcohol is a polyhydric alcohol.
12. A bleaching agent for teeth as claimed in any one of claims 3 to 11, wherein the bleaching agent for teeth further comprises 0.5 to 20% by weight of a thickener.
13. A bleaching agent for teeth as claimed in any one of claims 3 to 12, wherein the bleaching agent for teeth further



comprises 1 to 20% by weight of hydrogen peroxide.

14. A bleaching agent for teeth as claimed in any one of claims 3 to 13, wherein the bleaching agent for teeth further comprises 2 to 45% by weight of urea peroxide.

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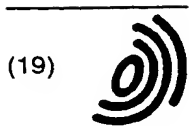
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### (54) Photocatalytic bleaching agent for teeth and method

(57) A method for bleaching teeth comprises steps of applying a solution containing nitrogen-doped titanium oxide powder on a surface of teeth, and irradiating the applied part with light to bleach the teeth based on a photocatalytic action thus produced, and a bleaching agent for teeth suitable for carrying out the method comprises a solution containing nitrogen-doped titanium oxide powder, in which the nitrogen-doped titanium oxide is preferably a photocatalytic substance having a Ti-O-N structure having a titanium oxide crystalline lattice containing nitrogen and exhibiting a photocatalytic action in

a visible light region, the bleaching agent contains preferably 0.01 to 5% by weight of the nitrogen-doped titanium oxide powder, the nitrogen-doped titanium oxide powder has a specific surface area of from 10 to 500 m<sup>2</sup>/g, the solution contains water and/or an alcohol as a solvent, and the bleaching agent further contains preferably 0.5 to 20% by weight of a thickener, 1 to 20% by weight of hydrogen peroxide, and 2 to 45% by weight of urea peroxide.

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## EUROPEAN SEARCH REPORT

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Place of search MUNICH		Date of completion of the search 7 January 2004	Examiner Werner, S
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